

filtered and the combined filtrates were reduced to dryness under reduced pressure. The residue was dissolved in hot benzene and was filtered to remove sulfur. The filtrate was chromatographed on 20 g of silica gel, 60–200 mesh (Davison Chemical Co.). Elution with benzene removed sulfur readily and subsequent elution with 3:1 benzene–ethyl acetate removed 274 mg of a slightly yellow oil. This material was evaporatively distilled at a bath temperature of 120°, 0.1 mm. The product obtained was 150 mg (28%) of yellow oil: $[\alpha]^{25D} -5.4 \pm 1.3$ (*c* 1.49, CHCl₃); infrared bands 3275, 1540, 1120, and 1160 cm⁻¹. In methanol the material was dextrorotatory at the sodium D line. The ORD data are reported in Table III.

Anal. Calcd for C₁₀H₁₀F₃NO: C, 51.49; H, 4.32; N, 6.00. Found: C, 51.40; H, 4.39; N, 6.17.

N-Methyl- α -ethyl-*p*-methoxyphenylthionacetamide (N-Methyl-2-*p*-methoxyphenylbutanthionamide).—The acid chloride, prepared from thionyl chloride and α -ethyl-*p*-methoxyphenylacetic acid, 1.0 g, $[\alpha]^{20D} +5.36$, enantiomeric purity 8.5%, was treated with 40% aqueous methylamine, 2 ml and the amide was isolated by washing the benzene layer successively with water, sodium bicarbonate solution, and saturated salt solution. The benzene layer was dried (MgSO₄) and evaporated to dryness, and the residue was recrystallized from petroleum ether (bp 77–110°) to give a product, 0.90 g, mp 97–100°, $[\alpha]^{20D} +3.3 \pm 0.5$ (EtOH, *c* 2). Since the yield of this material is 78%, the enantiomeric purity must be 8.5 \pm 2%.

This N-methylamide, 507 mg, was treated with sulfurated potash, 302 mg, and phosphorus pentasulfide, 363 mg, in xylene, 10 ml, by heating to 70–80° over a 15-min period and holding the temperature at this value for 60 min. The soluble portion was decanted and the residue was heated with a fresh portion of xylene at 110° for 30 min. The xylene mixture was filtered, and the filtrate was combined with the previous xylene solution and evaporated to dryness to give 546 mg of a mixture of oil and solid. Since this contained a small band in the infrared spectrum at 1625 cm⁻¹ indicative of unreacted amide, this crude product was again treated with sulfurated potash, 200 mg, and phosphorus pentasulfide, 245 mg, in xylene at 100° for 45 min. Isolation as before, followed by chromatography on silica gel, gave an oil which was further purified by evaporative distillation

at 160° (1 mm) to give 203 mg (38% yield). The infrared spectrum of this material was essentially identical with that of the crude initial product and the second reaction period may not have been necessary. The ORD data are reported in Table III.

(S)-(+)- α -Ethyl-*p*-methoxyphenylacetamide [(S)-(+)-2-*p*-Methoxyphenylbutanamide].—Ethyl-*p*-methoxyphenylacetic acid, $[\alpha]^{20D} +63.25$, 0.850 g, was refluxed with thionyl chloride, 2 ml, for 1 hr and the excess thionyl chloride was thoroughly removed under reduced pressure. The residue was dissolved in benzene, 10 ml, and into half of this solution was bubbled anhydrous ammonia. The precipitate was removed by filtration and digested with hot benzene; the combined benzene extracts were concentrated to dryness. The residue, 4.2 g, was twice recrystallized from petroleum ether (bp 60–80°) to give a product mp 111–113°, $[\alpha]^{24D} +23.0 \pm 0.8$ (absolute ethanol, *c* 1).

Anal. Calcd for C₁₁H₁₅NO₂: C, 68.37; H, 7.82. Found: C, 68.16; H, 7.83.

(S)-(+)- α -Ethyl-*p*-methoxyphenylacetanilide [(S)-(+)-2-*p*-Methoxyphenylbutanilide].—To the other half of the above benzene solution of the acid chloride was added 0.4 ml of aniline. Upon cooling the solution was filtered and the precipitate of aniline hydrochloride extracted with warm petroleum ether. The solution was evaporated to dryness (1 mm, 80°) and the residue was twice crystallized from petroleum ether (bp 60–80°) to give the purified anilide, 0.33 g, mp 125–127°, $[\alpha]^{24D} +80.0 \pm 0.8$ (absolute ethanol, *c* 2.75).

Anal. Calcd for C₁₇H₁₉O₂N: C, 75.81; H, 7.11. Found: C, 75.76; H, 7.10.

Registry No.— α -Trifluoromethylphenylacetaldehyde 2,4-DNPH, 13491-12-8; (–)- α -isopropylphenylacetic acid, 13491-13-9; α -isopropylphenylacetic acid cinchonidine salt, 13491-14-0; (–)- α -*t*-butylphenylacetic acid, 13491-16-2; (–)- α -trifluoromethylphenylacetic acid (+)- α -phenylethylamine salt, 13491-15-1; (–)- α -trifluoromethylphenylacetic acid, 13491-17-3; α -ethyl-*p*-methoxyphenylacetic acid cinchonidine salt, 13491-18-4.

Infrared Frequency Shifts of Phenol Owing to Hydrogen Bonding with Substituted Aromatics^{1,2}

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The frequency shifts $\Delta\nu_{OH}$ of phenol owing to hydrogen bonding with the ring π electrons of a number of mono- and polysubstituted benzenes and naphthalenes relate linearly with $\Sigma(\sigma_m + \sigma_p)/2$, rather than with $\Sigma\sigma_p$, suggesting a random orientation of the weak complex between phenol and π bases. The $\Delta\nu$ vs. $\Sigma(\sigma_m + \sigma_p)/2$ relation is not disturbed even when aromatic bases like hexaethylbenzene are used, so that it offers a simple method of estimating approximate $\sigma_m + \sigma_p$ values of the alkyl substituents. N-alkylanilines and 2,6-di-*t*-butylphenols were found to act solely as π bases in dilute carbon tetrachloride solution.

It has often been observed that aryl ethers^{3,4} and N,N-dimethylaniline^{4,5} act as the bifunctional proton acceptors in hydrogen bonding. The two donor sites have been estimated to be the ring π electrons and the lone-pair electron on oxygen or nitrogen atom. Recently, Wayland and Drago⁶ confirmed this assignment

by demonstrating, for the adducts between phenol and a number of monosubstituted benzenes in CCl₄ solutions, two linear relations between $\Delta\nu_{OH}$ (π) of phenol and σ_p of the substituent on the benzene ring and between $\Delta\nu_{OH}$ (n) and $\Sigma\sigma^*$ of substituents bonded to O or S atoms.

In view of the abundant evidence^{1,2,7,8} that X–H group lies near the center of the benzene ring with a certain degree of the thermal movement in the π -hydrogen bond complex, the use of σ_p constants in one of the Wayland–Drago relations ($\Delta\nu_{OH}$ (π) vs. σ_p) does not seem to be the best choice, since it implies the localization of phenol on the *para* or *ortho* carbon of the

(1) Part III of the series Intermolecular Hydrogen Bond Involving a π -Base as the Proton Acceptor.

(2) (a) Part II: Z. Yoshida and E. Ōsawa, *J. Am. Chem. Soc.*, **87**, 1467 (1965). (b) Part IV: Z. Yoshida, and E. Ōsawa, *ibid.*, **88**, 4019 (1966).

(3) R. West, L. S. Whatley, and K. J. Lake, *J. Am. Chem. Soc.*, **83**, 761 (1961).

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benzene ring of the proton acceptor. This consideration prompted us to study the OH frequencies of phenol interacted with a wide range of the substituted benzenes and naphthalenes in carbon tetrachloride solution. The data could be interpreted in terms of the combined substituent constants.

Experimental Section

Most of the reagents were commercial products purified by the usual methods. Hexaethylbenzene (Eastman Kodak Co.) was used without purification. Commercial 2,6-di-*t*-butyl-*p*-cresol was recrystallized twice from methanol, mp 70–71°. *p*-Di-*t*-butylbenzene was obtained as a by-product of the *t*-butylbenzene synthesis by the Friedel-Crafts alkylation of benzene with *t*-butyl alcohol;⁹ the distillation residue of *t*-butylbenzene was left standing for 6 months, the resulting crystals separated by filtration and recrystallized from ether, mp 77–78° (lit.¹⁰ mp 76–77.5°). β -Fluoronaphthalene¹¹ and N,N,2,6-tetramethylani-line¹² were prepared by the known methods.

The OH stretching frequency of phenol in solution of the substituted aromatics in carbon tetrachloride were recorded on a double-pass grating infrared spectrophotometer, Model 402-G, of Japan Spectroscopic Co. The procedure for the spectral measurements has been described before.^{1,2} The spectral slit width at 3600–3200 cm⁻¹ was kept at 1.7–3.0 cm⁻¹. Most of the spectra were taken using the 2-mm cells with rock salt plates. For each pair of a phenol and an aromatic, the dependence of $\Delta\nu_{OH}$ on the concentration of the proton acceptor¹³ was checked by varying the base concentration. When alkylbenzenes were used as the acceptor, the bonded OH frequencies were virtually invariant. With other substituents, however, appreciable variation of $\Delta\nu_{OH}$ with base concentration was often observed. In those cases, the final $\Delta\nu_{OH}$ value was obtained by extrapolating the proton acceptor concentration to infinite dilution. Error limits of the $\Delta\nu$ determination were estimated to be ± 2 cm⁻¹ for the sharp absorption band ($\Delta\nu \leq 100$ cm⁻¹) and ± 8 cm⁻¹ for the broader bands ($\Delta\nu \geq 100$ cm⁻¹).

When the following compounds were used as the proton acceptors, only a broad and largely shifted bonded OH band of phenol corresponding to O-H... π -electron interaction was observed: acetophenone, safrole, isosafrole, methyl cinnamate, benzaldehyde, methyl phenylacetate, benzonitrile, methyl *p*-toluenesulfonate, phenyl acetate, and styrene oxide. Methyl benzoate caused appearance of doublet bonded OH band centered at 3460 and 3393 cm⁻¹, both of which are due to the O-H...O interactions.¹⁴ The free OH absorption band of phenol at 3611 cm⁻¹ became slightly unsymmetrical when *p*-methoxybenzaldehyde was added to the carbon tetrachloride solution of phenol, although no attempt was made to resolve the unsymmetrical band. When halobenzenes were used as the proton acceptors, a shoulder appeared on the lower frequency side of the OH band of phenol, which was resolved mathematically (the Lorentz function).^{1,2}

Results and Discussion

The hydrogen bond shift data for the phenol-aromatic system are summarized in Tables I and II. *p*-Methoxyazobenzene, having three kinds of basic centers π , O, and N, expectedly caused quartet split of OH stretching spectra of phenol as shown in Figure 1. Assignment was made as shown from comparison of the shift data with anisole and azobenzenes. According to Wayland and Drago, $\Delta\nu_{OH}$ (π) data were plotted against $\Sigma\sigma_p$ of the substituents on the proton-accepting ring. As seen in Figure 2, there is a re-

TABLE I
PHENOL FREQUENCY SHIFTS^a AND HAMMETT SUBSTITUENT
CONSTANTS^b FOR SUBSTITUTED BENZENES

| Compd no. | Proton acceptors | $\Delta\nu_{OH}$, cm ⁻¹ | | $(\sigma_m + \sigma_p)/2$ |
|--------------|--|-------------------------------------|-----------------------|-------------------------------|
| | | π | n | |
| 1 | C ₆ H ₆ | 49 ^{c,d} | ... | 0 |
| 2 | C ₆ H ₅ CH ₃ | 58 ^c , 56 ^d | ... | -0.119 |
| 3 | C ₆ H ₄ (CH ₃) ₂ (<i>o</i>) | 68 ^c | ... | -0.240 |
| 4 | C ₆ H ₄ (CH ₃) ₂ (<i>m</i>) | 69 ^c | ... | -0.240 |
| 5 | C ₆ H ₄ (CH ₃) ₂ (<i>p</i>) | 69 ^c | ... | -0.240 |
| 6 | C ₆ H ₃ (CH ₃) ₃ (1,2,4) | 78 | ... | -0.360 |
| 7 | C ₆ H ₃ (CH ₃) ₃ (1,3,5) | 78 ^c | ... | -0.360 |
| 8 | C ₆ H ₂ (CH ₃) ₄ (1,2,4,5) | 85 ^c | ... | -0.480 |
| 9 | C ₆ H(CH ₃) ₅ | 99 | ... | -0.600 |
| 10 | C ₅ (CH ₃) ₅ | 106 ^c | ... | -0.720 |
| 11 | C ₆ H ₅ C ₂ H ₅ | 59 ^c | ... | -0.097 |
| 12 | C ₆ H ₄ (C ₂ H ₅) ₂ (mixt) ^e | 70 | ... | -0.194 |
| 13 | C ₆ H ₃ (C ₂ H ₅) ₃ (1,3,5) | 78 | ... | -0.291 |
| 14 | C ₆ H ₃ (C ₂ H ₅) ₃ (mixt) ^f | 77 | ... | -0.291 |
| 15 | C ₆ (C ₂ H ₅) ₆ | 97 | ... | -0.582 |
| 16 | C ₆ H ₅ CH(CH ₃) ₂ | 55 ^c | ... | (-0.03) |
| 17 | C ₆ H ₄ [CH(CH ₃) ₂] ₂ (mixt) ^g | 69 | ... | (-0.25) |
| 18 | CH ₃ C ₆ H ₄ CH(CH ₃) ₂ (<i>p</i>) | 72 | ... | (-0.30) |
| 19 | C ₆ H ₅ C(CH ₃) ₃ | 60 ^c | ... | -0.158 |
| 20 | CH ₃ C ₆ H ₄ C(CH ₃) ₃ (<i>p</i>) | 72 | ... | -0.278 |
| 21 | C ₆ H ₄ [C(CH ₃) ₃] ₂ (<i>p</i>) | 73 | ... | -0.316 |
| 22 | C ₆ H ₃ (CH ₃) ₄ (1,2) | 70 | ... | (-0.26) |
| 23 | C ₆ H ₅ C ₆ H ₁₁ (cyclo) | 64 | ... | (-0.17) |
| 24 | C ₆ H ₅ C ₁₂ H ₂₅ | 62 ^c | ... | (-0.14) |
| 25 | C ₆ H ₅ OCH ₃ | 54, 58 ^d | 150, 165 ^d | -0.077 |
| 26 | C ₆ H ₄ (OCH ₃) ₂ (<i>m</i>) | 69 | 167 | -0.154 |
| 27 | C ₆ H ₄ (OCH ₃) ₂ (<i>p</i>) | 54 | 157 | -0.154 |
| 28 | C ₆ H ₃ (OCH ₃) ₃ (1,3,5) | 64 | 146 | -0.231 |
| 29 | CH ₃ C ₆ H ₄ OCH ₃ (<i>p</i>) | 68 | 175 | -0.196 |
| 30 | ClC ₆ H ₄ OCH ₃ (<i>o</i>) | 26 | 89 | +0.223 +0.451 ^h |
| 31 | ClC ₆ H ₄ OCH ₃ (<i>p</i>) | 37 | 145 | +0.223 |
| 32 | C ₆ H ₅ OC ₂ H ₅ | 58 ⁱ | 163 ⁱ | -0.050 |
| 33 | C ₆ H ₄ (OC ₂ H ₅) ₂ | 71 | 189 | -0.100 |
| 34 | O ₂ NC ₆ H ₄ OC ₂ H ₅ (<i>p</i>) | ... | 93 | +0.694 |
| 35 | C ₆ H ₅ SCH ₃ | 49 ^{d,j} | 160, 170 ^d | +0.048 |
| 36 | CH ₃ C ₆ H ₄ SCH ₃ (<i>p</i>) | 59 ^j | 173 ^j | -0.071 |
| 37 | ClC ₆ H ₄ SCH ₃ (<i>p</i>) | 33 ^j | 151 ^j | +0.348 |
| 38 | C ₆ H ₅ OC ₆ H ₅ | 54, 52 ^d | 119, 125 ^d | (0.0) |
| 39 | C ₆ H ₅ CH ₂ OCH ₂ C ₆ H ₅ | 56 ⁱ | 237 ⁱ | (-0.05) |
| 40 | C ₆ H ₅ SC ₆ H ₅ | 42 ^j | 141 ^j | (+0.17) |
| 41 | C ₆ H ₅ SC ₆ H ₄ CH ₃ (<i>p</i>) | 43 ^j | 141 ^j | (+0.15) |
| 42 | C ₆ H ₅ SC ₆ H ₄ Cl (<i>p</i>) | 53 ^j | 128 ^j | (0.0) |
| 43 | C ₆ H ₅ C ₆ H ₅ | 52 ^c | ... | +0.113 |
| 44 | C ₆ H ₄ (C ₆ H ₅) ₂ (<i>o</i>) | 52 ^c | ... | +0.225 |
| 45 | C ₆ H ₄ (C ₆ H ₅) ₂ (<i>m</i>) | 56 ^c | ... | +0.225 |
| 46 | Indene | 57 | ... | (-0.06) |
| 47 | C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅ | 59 | ... | (-0.10) |
| 48 | C ₆ H ₅ NCS | 20 | 85 | ... |
| 49 | C ₆ H ₅ NCO | 31 | (180) | ... |
| 50 | C ₆ H ₅ NHCH ₃ | 73 | ... | -0.447 |
| 51 | C ₆ H ₅ N(CH ₃) ₂ | 70 | ... | -0.406 |
| 52 | C ₆ H ₅ N(C ₂ H ₅) ₂ | 76, 67 ^k | ... | (-0.36) |
| 53 | C ₆ H ₅ N(C ₆ H ₅) ₂ | 82 | ... | (-0.45) |
| 54 | CH ₃ C ₆ H ₄ N(CH ₃) ₂ (<i>o</i>) | 73 | l | -0.525 -0.330 ^m |
| 55 | CH ₃ C ₆ H ₄ N(CH ₃) ₂ (<i>m</i>) | 90 | ... | -0.525 |
| 56 | CH ₃ C ₆ H ₄ N(CH ₃) ₂ (<i>p</i>) | 86 | ... | -0.525 |
| 57 | CH ₃ C ₆ H ₄ N(C ₆ H ₅) ₂ (<i>m</i>) | 93 | ... | (-0.62) |
| 58 | (CH ₃) ₂ C ₆ H ₃ N(CH ₃) ₂ (2,6) | 78 | l | -0.644 -0.451 ⁿ |
| 59 | C ₆ H ₅ N=NC ₆ H ₅ | 45 | 274 | (+0.12) |
| 60 | C ₆ H ₅ N=NC ₆ H ₄ NH ₂ (<i>p</i>) | 51 | ... | ... |
| 61 | C ₆ H ₅ N=NC ₆ H ₄ OCH ₃ (<i>p</i>) | 49 | 156, 311 | ... |
| 62 | CH ₃ C ₆ H ₄ N=NC ₆ H ₄ CH ₃ (<i>m, m'</i>) | 49 | 297 | ... |
| 63 | CH ₃ C ₆ H ₄ N=NC ₁₀ H ₆ NH ₂ (<i>o, o'</i>) | 52 | ... | ... |
| 64 | C ₆ H ₅ CH=NC ₆ H ₅ | 45 | 435 | ... |
| 65 | HOC ₆ H ₄ [C(CH ₃) ₃] ₂ (2,6) | 77 | ... | -0.496 |
| 66 | HOC ₆ H ₂ (CH ₃) ₂ [C(CH ₃) ₃] ₂ (4,2,6) | ... | ... | 0.614 |
| 67 | C ₆ H ₅ F | 38 | ... | +0.199 |
| 68 | C ₆ H ₅ Cl | 33, 39 ^d | ... | +0.300 |
| 69 | C ₆ H ₅ Br | 37, 40 ^d | ... | +0.311 |
| 70 | C ₆ H ₅ I | 38 | ... | +0.314 |

^a Phenol $\nu_{OH} = 3611$ cm⁻¹. ^b H. H. Jaffé, *Chem. Rev.*, **53**, 222 (1953). ^c See ref 2b. ^d See ref 6. ^e *o*:*m*:*p* = 1:3:6 (vpc).

^f A mixture of two components 4:5 (vpc). ^g *m*:*p* = 2:1 (vpc). ^h $(\sigma_m^{Cl} - \sigma_p^{Cl})/2 + \sigma_m^{OCH_3}$. ⁱ Z. Yoshida and E. Ōsawa, unpublished results. ^j Z. Yoshida and H. Miyoshi, unpublished results. ^k T. Gramstad, *Acta Chem. Scand.*, **16**, 807 (1962). ^l Very weak and broad absorption centered at around 3200 cm⁻¹. ^m $(\sigma_m^{CH_3} + \sigma_p^{CH_3})/2 + \sigma_m^{N(CH_3)_2}$. ⁿ $[2(\sigma_m^{CH_3} + \sigma_p^{CH_3})/2] + \sigma_m^{N(CH_3)_2}$.

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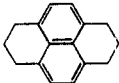
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(12) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 20 (1953).

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TABLE II
PHENOL FREQUENCY SHIFT^a AND HAMMETT SUBSTITUENT
CONSTANTS^b FOR SUBSTITUTED NAPHTHALENES

| Compd no. | Proton acceptors | -Δν _{OH} , cm ⁻¹ | | |
|-----------|---|--------------------------------------|-----|--------------------------------------|
| | | π | n | (σ _m + σ _p)/2 |
| 71 | C ₁₀ H ₈ (Naphthalene) | 48 ^c | ... | 0 |
| 72 | C ₁₀ H ₇ CH ₃ (α) | 53 ^c | ... | -0.119 |
| 73 | C ₁₀ H ₇ CH ₃ (β) | 54 ^c | ... | -0.119 |
| 74 | C ₁₀ H ₆ (CH ₃) ₂ (2,3) | 58 ^c | ... | -0.240 |
| 75 | C ₁₀ H ₆ (CH ₃) ₂ (2,6) | 59 ^c | ... | -0.240 |
| 76 | C ₁₀ H ₆ (CH ₃) ₂ (1,8) | 51 | ... | ... |
| 77 | C ₁₀ H ₆ (CH ₃) ₂ (1,8) | 58 ^c | ... | ... |
| 78 |  | 69 ^c | ... | ... |
| 79 | C ₁₀ H ₇ Cl (α) | 37 | ... | +0.300 |
| 80 | C ₁₀ H ₇ F (β) | 40 | ... | +0.199 |
| 81 | C ₁₀ H ₇ OCH ₃ (α) | 44 | 134 | -0.077 |
| 82 | C ₁₀ H ₇ OCH ₃ (β) | 45 | 134 | -0.077 |

^a Phenol ν_{OH} = 3611 cm⁻¹. ^b H. Jaffé, *Chem. Rev.*, **53**, 222 (1953). ^c See ref 1 and 2.

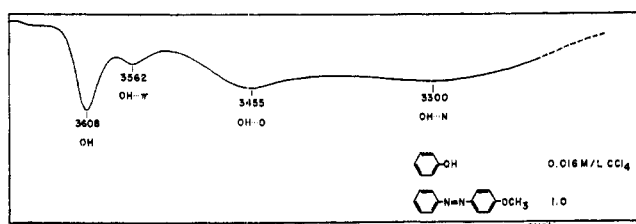


Figure 1.—Quartet OH stretching absorption spectra of phenol in solution of *p*-methoxyazobenzene in carbon tetrachloride.

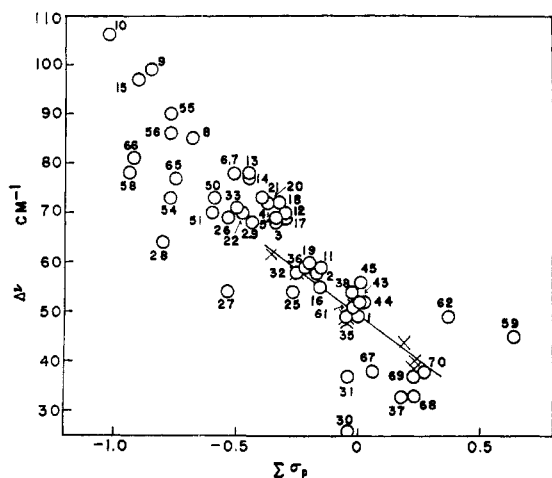


Figure 2.—The Δν_{OH} (π) vs. Σσ_p plot for phenol-substituted benzenes adducts in carbon tetrachloride. X taken from ref 6.

markable scattering. The linearity was appreciably improved when Δν_{O-H} (π) was plotted against Σ(σ_m + σ_p)/2 (cf. Table I) as shown in Figure 3.

The least-square treatment gave an empirical equation (eq 1). Large deviations are observed for the

$$\Delta\nu_{OH}(\pi) = [-62\Sigma(\sigma_m + \sigma_p)/2] + (53 \pm 9 \text{ cm}^{-1}) \quad (1)$$

points of *o*- and *m*-terphenyl (compounds 44 and 45), *o*-chloroanisole (30), *N,N*-dimethyl-*o*-toluidine (54), and *N,N*,2,6-tetramethylaniline (58), which are not taken into the least-square treatment. The reason for these deviations are not yet clear, but some rationalization seems possible. Terphenyls are likely to interact with phenol at the terminal rings both from statistical and

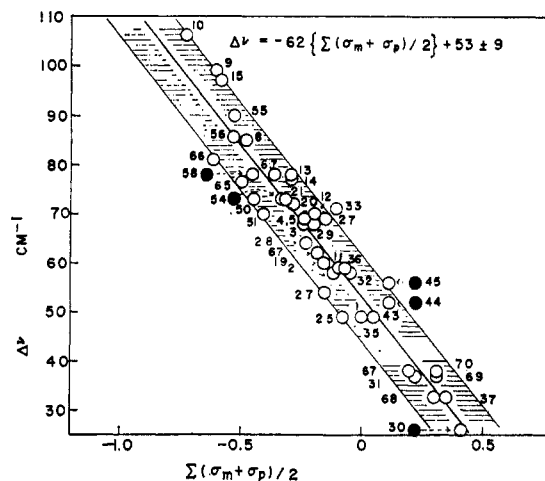


Figure 3.—The Δν_{OH} (π) vs. Σ(σ_m + σ_p)/2 plot for phenol-substituted benzene adducts in carbon tetrachloride.

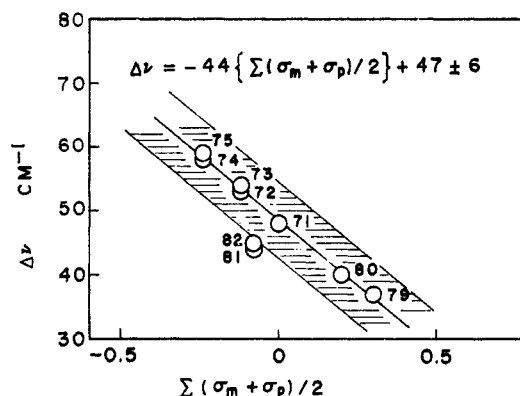


Figure 4.—The Δν_{OH} (π) vs. Σ(σ_m + σ_p)/2 plot for phenol-substituted naphthalene adducts in carbon tetrachloride.

steric reasons. The “biphenyl benzene” will be quite similar to biphenyl in hydrogen bonding behavior. Consequently, σ of one rather than two phenyl groups may be used here. With *ortho*-substituted methoxy and dimethylamino groups, which are rotated from the plane of benzene ring, (σ_m + σ_p)/2 could be replaced by σ_m constant. These corrections afford satisfactory fit to eq 1 as shown in Figure 3.

The Δν_{OH} (π) vs. Σ(σ_m + σ_p)/2 plots for the phenol-naphthalene derivative adducts are shown in Figure 4, where compounds 72 and 74 are assumed to be similar to 1,8-dimethyl and 1,4,5,8-tetraethylnaphthalene, respectively. Again a straight line (eq 2) was obtained.

$$\Delta\nu_{OH}(\pi) = [44\Sigma(\sigma_m + \sigma_p)/2] + (47 \pm 6 \text{ cm}^{-1}) \quad (2)$$

The result that the shift Δν_{OH} (π) was better correlated with the sum of σ_m and σ_p than with σ_p indicates that the hydrogen bond involves not only the π electron on the carbon atom *para* or *ortho* to the substituent but the whole π system. This is consistent with the conclusions obtained from our previous equilibrium studies^{1,2} as well as the nmr⁷ and X-ray⁸ results.

Although the error limits of eq 1 and 2 are fairly large (±6–9 cm⁻¹ with 90% confidence), estimation of an unknown σ_m + σ_p value from Δν_{OH} (π) is possible by the use of this equation. The insensitiveness of Δν_{OH} (π) to the steric crowding owing to alkyl groups attached to the ring (e.g., *p*-di-*t*-butylbenzene (21) and hexaethylbenzene (15)) lends a practical utility to the

estimation.¹⁵ Some of the estimated $\Sigma(\sigma_m + \sigma_p)/2$ values are included in Table I in parentheses. The estimation is reliable to within a ± 0.1 -unit variation. The hydrogen-bonding interaction to the naphthalene ring appears to involve all ten π electrons since eq 2 holds regardless of the position of the substituents on the ring. This result again agrees with our earlier work.^{2b}

The ν_{OH} spectra of phenol in solutions of N-alkylanilines (50–57) in carbon tetrachloride were not the expected triplet, but always a doublet. The lower frequency band of the doublet corresponds to the OH interacting with the π electron of the ring, because the $\Delta\nu_{OH}$ vs. $\Sigma(\sigma_m + \sigma_p)/2$ plot fell on the correlation line in Figure 2. The very weak and broad band at about 3400–3300 cm^{-1} owing to X–H \cdots N interaction does not appear until phenols³ or pyrrole⁴ are dissolved in the neat liquid N,N-dimethylaniline. Evidently, the O–H \cdots π type of interaction is much more favored than the O–H \cdots N interaction in phenol-N-alkylaniline adducts, although the hydrogen bond shift is much larger for the latter than for the former. Steric inhibition of the n – π resonance in the anilines causes the O–H \cdots n band to appear; a very weak and broad band centered at about 3200 cm^{-1} was observed when the proton accepting N,N-dialkylaniline has a methyl group in the *ortho* position (54 and 58). It is interesting to note that the protonation of N-alkylanilines in strong acid medium occurs also only on the nitrogen atom.¹⁶

The behavior of the oxygenated benzenes furnishes an interesting contrast with the N-alkylbenzenes; mono- and polyalkoxybenzenes (25–33) and thioalkoxy-

(15) Effect of the steric crowding appears itself in the equilibrium constant. The K for the phenol-hexamethylbenzene adduct is anomalously low.^{2b} Hexaethylbenzene is a well-quoted example of sterically hindered π donor in CT complex: T. W. Nakagawa, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **82**, 269 (1960).

(16) W. Koch, private communication; also cf. T. Isobe, T. Ikenoue, and G. Hazato, *J. Chem. Phys.*, **30**, 1371 (1959).

benzenes (35–37) act as bifunctional donors in hydrogen bonding, while in HSO_2F and HF-BF_3 they protonate exclusively on the ring carbon.¹⁷ When the lone-pair electron on oxygen is hindered by two *t*-butyl groups in *ortho* position (65 and 66), the $\text{OH}\cdots\text{O}$ absorption band disappears and only the $\text{OH}\cdots\pi$ band was observed even if 0.5 M of the 2,6-di-*t*-butyl phenols were added to 0.016 M of phenol.¹⁸

Registry No.—1, 71-43-2; 2, 108-88-3; 3, 95-47-6; 4, 108-38-3; 5, 106-42-3; 6, 95-63-6; 7, 108-67-8; 8, 95-93-2; 9, 700-12-9; 10, 87-85-4; 11, 100-41-4; 12 (*o*), 135-01-3; 12 (*m*), 141-93-5; 12 (*p*), 105-05-5; 13, 102-25-0; 15, 604-88-6; 16, 98-82-8; 17 (*m*), 99-62-7; 17 (*p*), 100-18-5; 18, 99-82-1; 19, 98-06-6; 20, 98-51-1; 21, 1012-72-2; 22, 119-64-2; 23, 827-52-1; 24, 123-01-3; 25, 100-66-3; 26, 151-10-1; 27, 150-78-7; 28, 621-23-8; 29, 104-93-8; 30, 766-51-8; 31, 623-12-1; 32, 103-73-1; 33, 122-95-2; 34, 100-29-8; 35, 100-68-5; 36, 623-13-2; 37, 123-09-1; 38, 101-84-8; 39, 103-50-4; 40, 139-66-2; 41, 3699-01-2; 42, 13343-26-5; 43, 92-52-4; 44, 84-15-1; 45, 92-06-8; 46, 95-13-6; 47, 103-29-7; 48, 103-72-0; 49, 103-71-9; 50, 100-61-8; 51, 121-69-7; 52, 91-66-7; 53, 613-29-6; 54, 609-72-3; 55, 121-72-2; 56, 99-97-8; 57, 91-67-8; 58, 769-06-2; 59, 103-33-3; 60, 60-09-3; 61, 2396-60-3; 62, 588-04-5; 63, 131-79-3; 64, 538-51-2; 65, 128-39-2; 66, 128-37-0; 67, 462-06-6; 68, 108-90-7; 69, 108-86-1; 70, 591-50-4; 71, 91-20-3; 72, 90-12-0; 73, 91-57-6; 74, 581-40-8; 75, 581-42-0; 76, 208-96-8; 77, 83-32-9; 78, 1732-13-4; 79, 90-13-1; 80, 323-09-1; 81, 2216-69-5; 82, 93-04-9; phenol, 108-95-2.

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(17) T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Can. J. Chem.*, **42**, 1433 (1964). In aqueous H_2SO_4 and HClO_4 , O protonation was observed to occur to a small extent: A. J. Kresge and L. E. Hakka, *J. Am. Chem. Soc.*, **88**, 3868 (1966).

(18) Note that di-*t*-butyl ether forms a hydrogen bond with phenol under similar conditions: R. West, D. L. Powell, M. K. T. Lee, and L. S. Whatley, *ibid.*, **86**, 3227 (1964).

The Hydrolysis of Some Monophenyl Phosphates¹

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There is a linear free-energy relation between $\log k_{\nu}$ for hydrolysis of monoanions of monoalkyl or -aryl phosphates and $\text{p}K$ of the alcohol or phenol, with a slope of approximately 0.3. Bulky *ortho* substituents hinder hydrolysis slightly. Acid-catalyzed hydrolyses are observed only with the nitrophenyl phosphates, with rate maxima at approximately 5 M acid. Hydrolyses of the undissociated nitrophenyl phosphates are important, especially at low temperatures with the *ortho* and *para* isomers.

The hydrolysis of a simple aryl phosphate involves phosphorus-oxygen bond fission and the most important reactive species is the monoanion ArOPO_3H^- .³

(1) This work was presented in part at the Symposium on Bio-Organic Reactions, Western Regional Meeting of the American Chemical Society, Los Angeles, Nov 19, 1965, and is abstracted in part from the theses of E. J. Fendler and K.-U. Yang, submitted in partial fulfillment of the respective requirements of the degrees of Doctor of Philosophy and Master of Arts of the University of California at Santa Barbara. It was supported by grants from the National Science Foundation and the National Institute of Arthritis and Metabolic Diseases. This support is gratefully acknowledged.

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Acids catalyze the hydrolyses of *p*-nitro- and *p*-acetylphenyl phosphates in water, with a maximum reaction rate at approximately 5 M acid.^{3–5} One aim of the present work was to find out whether the presence of a *m*-nitro group would lead to a similar rate maximum in acid. There is also some rate increase at high pH, probably caused by a reaction between hydroxide ion and the dianion ArOPO_3^{2-} .⁶ This reaction becomes

(3) P. W. C. Barnard, C. A. Bunton, D. Kellerman, M. M. Mhala, B. Silver, C. A. Vernon, and V. A. Welch, *J. Chem. Soc., Sect. B*, 227 (1966).

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(6) A. J. Kirby and W. P. Jencks, *J. Am. Chem. Soc.*, **87**, 3209, 3217 (1965).